Liquid processible, thermally stable, hydrophobic phenolic-triazine resins for advanced composite applications.

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Abstract

Composite structures are seeing demand for higher temperature performance and thus there is a need for advanced resin systems to meet this requirement. Here a commercial phenolic-triazine (PT) resin is combined with a blend of low viscosity difunctional cyanate ester (Primaset^{TM} LECy) to achieve a series of reactive binary systems. Throughout this work, the properties of the blends are compared against an industrial standard (Primaset^{TM} PT-30). The thermomechanical performances of the cured blends compare favourably with the industrial standard system with the best performing systems exhibiting T_g values in excess of 300 °C, based on the drop in storage modulus (compared with a value of at least 350 °C for PT-30). After conditioning for 3127 hours at 80 °C and 85% RH, a cured binary resin blend absorbed 4.9 wt% of moisture, compared with a figure of 5.2 wt % for PT-30. When exposed to 250 ºC in air continuously over a period of 3048 hours, the best performing of the binary cured blends lose only 48.3 % of their mass, compared with 45.0 % for PT-30 under the same conditions. The importance of this work is that the newly proposed resin blends containing 20 to 25 wt% LECy exhibit low viscosities (<1000 mPa.s) at 50 °C and are considerably more suitable for liquid composite moulding

processes when compared with the state-of-the-art commercial matrix, while showing improved moisture performance, with only minimal loss in thermal performance.

KEYWORDS: cyanate ester; PT resins; high temperature; liquid processable; thermoset polymers.

1 Introduction

Advanced carbon fibre reinforced plastic (CFRP) composites offer unparalleled specific strength and stiffness when compared with metallic components [1], but care must be exercised when selecting the polymers to fulfil the role of organic matrices in the engineering materials. When designing complex, high performance aerospace components produced from CFRP, the demands of the application are of paramount importance and where high thermal stability and mechanical strength are key requirements, thermoset polymer matrices are commonly used [2]. At the more modest operating temperatures experienced in secondary applications in civil aviation (*i.e.* with continuous service conditions up to 121 ºC/250 ºF with short duration spikes up to 204 ºC/400 ºF), epoxy/CFRP components produced from di- and tri-functional epoxy monomers are perfectly capable of prolonged service lives, when cured with aromatic polyamines. Tetrafunctional epoxy resins [3] are also available, which extend the ceiling temperature further by offering higher glass transition temperatures, but as advanced composites are increasingly considered for more demanding environments, then conventional difunctional epoxy resins are no longer considered adequate.

Gas turbine engines are particularly demanding environments for any material, since they are designed to experience a wide range of conditions, including high stress, high temperature gradients, and hot/corrosive fluids. The need to increase thrust to weight ratio and minimise fuel consumption, as well as for stronger, stiffer, defect- and high temperature-tolerant components

has led to the increasing use of organic matrix composite materials in this application, since their first use in the RB162 lift jet engine almost 50 years ago [4]. The aluminium alloys that were used for the compressor blade, casing and impeller components were initially replaced by glass fibre reinforced plastic (GFRP), which offered components that were now twice as strong and 25% less dense [5]. However, in areas in which stiffness was critical to the application, designers turned to the use of CFRP, which displays higher specific strength than either aluminium or GFRP.

As ceiling temperatures rise, the choice of organic matrices becomes more limited [6] to the use of highly aromatic polymers, such as linear polyimides bearing reactive end caps [7] (*e.g.* PMR 15 [8] and its commercial successor DMBZ-15 which incorporates 2,2'-dimethylbenzidine [9], and PETI 330 [10]), or phenol-formaldehyde resins (phenolic novolacs) [11] and closely related phenyl aralkyl resins, and epoxy novolacs [12]. While a variety of other polymers have been offered [13] (*e.g.* bismaleimides [14,15], and most recently polybenzoxazines [16]), these have either proven to be more limited in terms of thermo-mechanical properties, thermo-oxidative stability, or have simply yet to achieve wider adoption in the more conservative industrial sectors, such as civil aerospace.

Of the more recent commercial offerings, phenolic-triazine (PT) resins, based on oligomers of cyanated novolacs, have become increasingly adopted where applications demand high glass transition temperatures (T_g) coupled with thermal stability [17]. Consequently, they are being considered in the production of CFRP components for gas turbine propulsion units, although their organic nature limits their (extended) use in air in more thermally critical areas to operating temperatures to below 250 ºC. PT resins are typically processed in prepreg form (pre-impregnated carbon tape) as their comparatively high viscosity (296 Pa.s at 72 ºC) renders it

impractical to process them in liquid form without the introduction of solvents, which might lead to porosity, void formation during the curing process, and the potential to accelerate depolymerisation in the cured network [18].

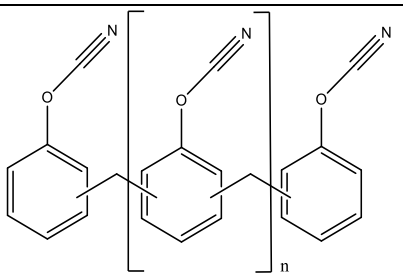
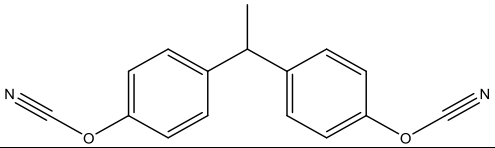
The aim of the present work is to combine a commercial PT oligomer with a second liquid cyanate ester monomer with the intention of producing liquid processable systems that are stable at room temperature, display increased thermal reactivity, while maintaining or improving upon the ultimate properties of the cured materials.

2 Experimental methods

2.1 Materials.

Primaset^{TM} PT-30, an oligomeric phenolic cyanate (average value of n = 1), (**1**) and Primaset^{TM} LECy (**2**) were purchased from Lonza AG (Visp, Switzerland) (Table 1) and were used as received (Table 1).

Table 1. The chemical structures of the monomers used in this work.

Chemical Name	Trade name	Number	Structure
Phenolic triazine oligomer	Primaset^{TM} PT-30	**1**	
1,1-bis(4-cyanatophenyl)ethane	Primaset^{TM} LECy	**2**	

For clarity, each monomer is assigned a number, by which it will be referred throughout. In the case of blends, the notation [$\mathbf{1}_x$:$\mathbf{2}_y$] is used, where **1** and **2** are the assigned monomer numbers and x and y are their corresponding weight percentages in the blend composition.

2.2 Formulation and curing of PT resins.

The binary blends were prepared by weighing **1** and **2** into a 100 ml reaction vessel (coated three times with Frekote 700-NC *ex* Loctite) in the desired ratios (ranging from 100:0 to 75:25 by weight) and stirred by hand at 125 °C for 2 minutes. The resulting homogeneous blends were poured into the desired mould, in which they were degassed for 20 minutes at 125 °C in a vacuum oven. Resins samples were cured in a convection oven using the following cure cycle, unless otherwise stated: 160 °C for 1 hour, 200 °C for 3 hours, and 250 °C for 1 hour. Owing to its viscosity, prior to weighing the Primaset^{TM} PT-30 (**1**) was heated to 90 °C for 30 minutes.

2.3 Fourier-transform infrared spectroscopy.

FTIR spectra of the blends were acquired using a PerkinElmer Spectrum 100 FTIR Spectrometer. The spectrum range was 4000-500 cm^{-1}, and 10 scans were run for each measurement. Prior to sample measurement, a background check was run to remove any interferences caused by the air, and the ATR was cleaned with an alcohol wipe.

2.4 Rheological analysis.

Rheology measurements were performed using a TA Discovery HR-1 hybrid rheometer instrument equipped with a parallel plate fixture. Disposable aluminium plates of 25 mm in diameter with a gap of 0.5 mm were used. To determine whether the shear rate influences the viscosity of the blends tested, a flow sweep test was performed at 35 °C with shear rate of 0.1 –

100.0 s^{-1}. This was followed by a temperature ramp programme. Samples were heated from room temperature to 130 °C (well below their gel point), at a heating rate of 5 °C min^{-1}. The strain frequency used was 1 Hz and an oscillation amplitude of 50 % was selected as this fell well within the linear viscoelastic regime.

2.5 Dynamic scanning calorimetry (DSC).

DSC experiments were performed using a TA DSC Q2000. Hermetically sealed Tzero aluminium pans were used, with sample masses of 6.0 ± 1.0 mg (uncured samples) and 5.1 ± 0.2 mg (cured samples). Sealing is required to prevent evaporation or sublimation from the pan. Samples were equilibrated at 30 °C and then heated to 375 °C at a heating rate of 10 °C min^{-1}, unless otherwise stated, with the sample cell kept under a constant nitrogen flow of 50 cm^3 min^{-1}. Heat/cool/heat scans, using a cooling rate of 10 °C min^{-1}., were employed to determine whether residual curing exotherms were present. DSC kinetics were studied, using heating rates of 5, 10, 15, and 20 °C min^{-1}.

2.6 Dynamic mechanical analysis (DMA).

DMA measurements were performed using a Netzsch DMA 242 instrument equipped with a 16 mm single cantilever bending fixture. Sample dimensions of the parallelepiped bars were 2 x 12 x 35 mm^3. Samples were heated from room temperature to 450 °C at a heating rate of 3 °C min^{-1}, with a displacement amplitude of 40 μm and a frequency of 1 Hz, under N_2 purge atmosphere of 50 cm^3 min^{-1}.

2.7 Simultaneous thermal analysis (STA).

STA measurements were performed using a Netzsch STA 449 F3 Jupiter instrument equipped with alumina sample pans. Experiments were undertaken on cured samples with masses of 7.0 ± 0.3 mg in a N_2 environment at a heating rate of 10 °K min^{-1}. Samples were equilibrated at 30 °C for 10 minutes and then heated to 800 °C at 10 °C.

2.8 Determination of thermo-oxidative stability.

Cured samples of each material (0.0150 ± 0.0020 g) were placed in a GenLab prime air circulating oven and held isothermally at 250 °C. Measurements of the samples' masses were recorded on a weekly basis.

2.9 Moisture uptake.

Moisture uptake measurements were performed on cured resins of dimensions 2 x 12 x 35 mm^3, using a Vötsch Industrietechnik VC 7034 moisture chamber. Conditions of 85 % RH at 80 °C were used, as dictated by the ASTM Standard [19]. Measurements of the samples' masses were recorded periodically, initially at short interval time periods for the first four days, followed by twice-weekly measurements.

3 Results and discussion

3.1 Preparation and properties of binary blends.

The cured resins based on binary [$\mathbf{1}_{80}$:$\mathbf{2}_{20}$] blends produced transparent, dark brown solids, and Koh *et al.* attributed the colour to thermal oxidation of the resin [20]. Infrared (IR) spectra were also obtained from both the upper and lower surfaces of all cured binary blends, exemplified by

[$\mathbf{1}_{90}$:$\mathbf{2}_{10}$] (see Supplementary data, **Error! Reference source not found.**). The spectral differences in the top provide evidence for the presence of unreacted cyanate esters at the bottom of the blends (notably the presence of the two peaks at 2257 and 2270 cm^{-1} due to the O-C≡N stretch [21]). When curing the samples, the top surface of the resins is exposed to the air in the oven. As a result, during the curing process moisture is trapped in the surface of the blend as evidenced by the presence of an -OH peak (3300 cm^{-1}), and not at its bottom. This observation could suggest that moisture in the air catalyses the reaction, however the high cure conversions suggest otherwise. Such an effect does not pose a threat for the composite manufacturing process, as composites are cured under vacuum, where the resin is not in contact with the moisture of the air. Note that the slope difference between 1700-500 cm^{-1} are attributed to poor contact between the sample and attenuated total reflectance (ATR) crystal, due to the shape of the mould where the resin was cured.

3.2 Examining the processability of the binary blends.

Resin processing techniques, such as resin transfer moulding (RTM), vacuum assisted resin injection moulding (VARIM), or wet filament winding (FW) require viscosities of 100-1000 mPa.s at the lowest possible temperature [21]. Higher viscosities result in non-uniform wetting, possible void formation, and poor mechanical properties in the cured laminate. Consequently, a low viscosity dicyanate ester monomer, derived from bisphenol E (**2**), was used as a reactive diluent to the more viscous phenolic triazine oligomer (**1**), as a means of achieving a lower viscosity prepolymer, which simplifies the manufacturing process and enables the resin to be more versatile in terms of its processing.

The benchmark material used in this study is (**1**) is a high performance cyanated novolac with a viscosity of 296 Pa.s at 30 °C and a dry T_g of 404 °C in the cured polymer. LECy (**2**) is a waxy monomer (a supercooled liquid), which remains molten when heated, until crystallites develop in the system, at which point it solidifies. The incorporation of LECy was tested at several compositions varying from [$\mathbf{1}_{100}$:$\mathbf{2}_{0}$] to [$\mathbf{1}_{75}$:$\mathbf{2}_{25}$]. Incorporation of LECy (**2**) resulted in a significant reduction in the viscosity of the binary blend: a two-fold drop in viscosity was achieved by addition of 5 wt % of LECy in [$\mathbf{1}_{95}$:$\mathbf{2}_{5}$] (149 Pa.s), while at 25 wt %, the viscosity dropped down to 9.6 Pa.s in [$\mathbf{1}_{75}$:$\mathbf{2}_{25}$] (Fig. 1).

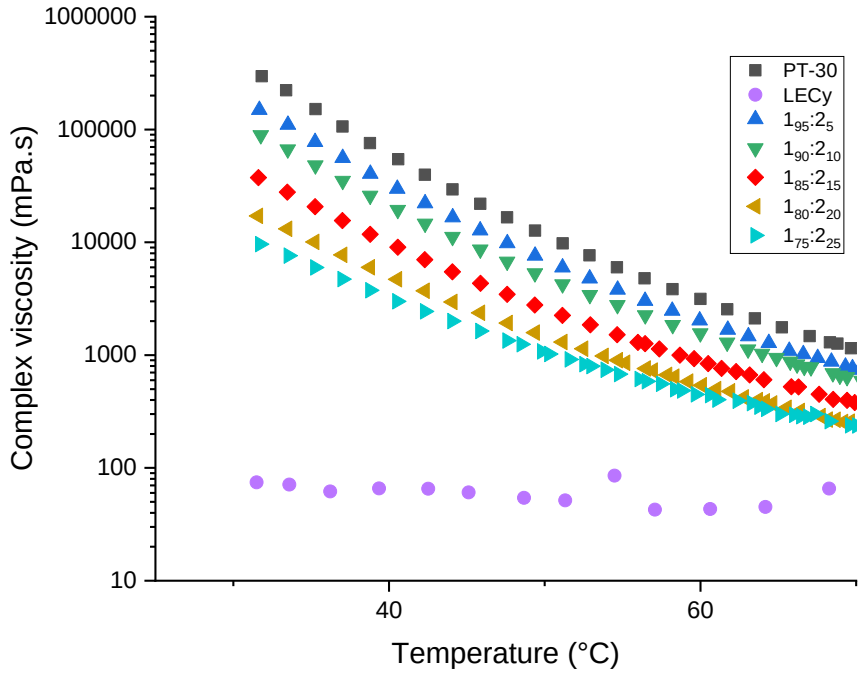


Figure 1: Semi-log of complex viscosity against temperature plot of binary [$\mathbf{1}_x$:$\mathbf{2}_y$] blends.

The processing temperatures were reduced by more than 10 °C *via* the incorporation of 15 wt % of LECy, resulting in a more simplified and cost-effective process (Table 2).

Table 2: A list of viscosity values at room temperature and minimum temperature at which liquid resin processing is possible

System	Complex viscosity (Pa.s) at 30 °C	Temperature at which complex viscosity reaches 1000 mPa.s (°C)
1	296	72
$\mathbf{1}_{95}\mathbf{2}_{5}$	149	68
$\mathbf{1}_{90}\mathbf{2}_{10}$	89	65
$\mathbf{1}_{85}\mathbf{2}_{15}$	37	59
$\mathbf{1}_{80}\mathbf{2}_{20}$	17	54
$\mathbf{1}_{75}\mathbf{2}_{25}$	10	52

3.3 Examining the thermal polymerisation of the binary blends.

The binary blends were analysed using differential scanning calorimetry (DSC) and the presence of single, bell shaped curves in the DSC thermograms of all blends confirm the simultaneous reaction of the components of the blends. These ring-forming reactions represent homopolymerization of the individual monomers (to form thermally stable polycyanurates), and the co-cyclotrimerization of two cyanate ester monomers, resulting in the formation of mixed polycyanurates. Binary blends comprising five different stoichiometries, ranging from $\mathbf{1}_{95}$:$\mathbf{2}_{5}$ to $\mathbf{1}_{75}$:$\mathbf{2}_{25}$ were blended and tested. The DSC data are provided in Table 3, and the DSC thermograms (Figure), are compared to (**1**) and (**2**).

Table 3: DSC data and degree of curing for cyanate ester binary blends of $\mathbf{1}_{x}$:$\mathbf{2}_{y}$

System	(T_o)	T_{exo}	ΔH_c	Curing enthalpy of cyanate equivalent	ΔH_{pc} (J/g)	α

	(°C)	(°C)	(J/g)	(kJ/mol OCN)		($1-\frac{\Delta H_{pc}}{\Delta_c}$)
1	188	284	581	73.9	24	0.96
2	219	315	1080	142.7	11.6	0.99
$\mathbf{1}_{95}\mathbf{2}_{5}$	221	299	512	65.2	16	0.97
$\mathbf{1}_{90}\mathbf{2}_{10}$	221	300	501	64.0	22	0.96
$\mathbf{1}_{85}\mathbf{2}_{15}$	206	287	638	81.5	22	0.97
$\mathbf{1}_{80}\mathbf{2}_{20}$	225	302	470	60.2	14	0.97
$\mathbf{1}_{75}\mathbf{2}_{25}$	221	301	444	57.0	16	0.96

Key: T_o = Temperature of onset of polymerization, T_{exo} = Exothermic peak temperature, ΔH_c = curing exotherm enthalpy, ΔH_{pc} = post curing exotherm enthalpy, α = degree of curing.

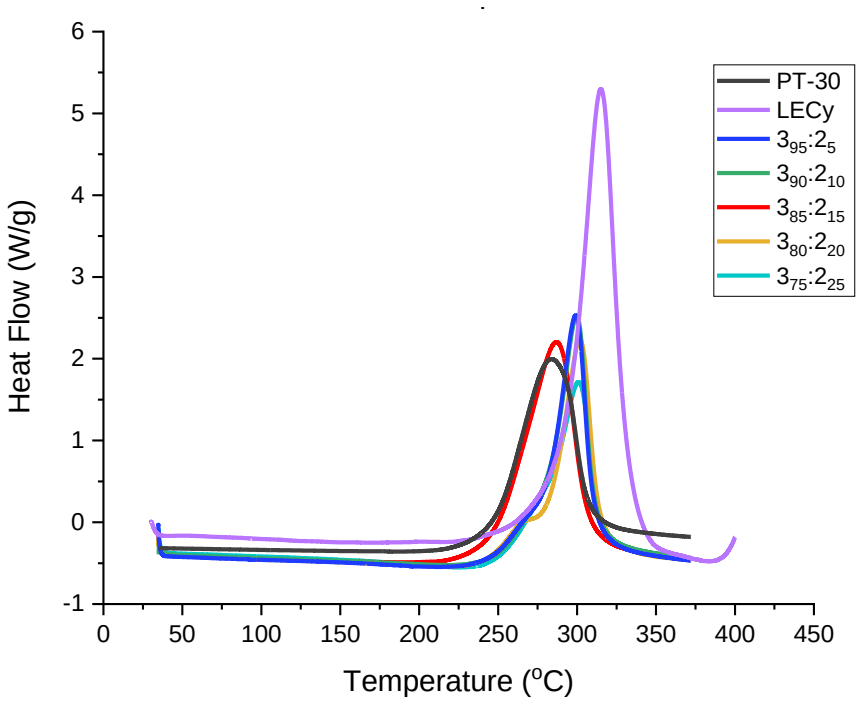


Figure 2: DSC thermograms of the uncured binary $\mathbf{1}_x$:$\mathbf{2}_y$ blends compared to PT-30 (**1**) and LECy (**2**)

Throughout the blends, the values of the onset of polymerisation (T_o), the temperature of the exothermic peak maximum (T_{exo}), and the value of the polymerization enthalpy (ΔH_c) remain relatively constant (Table 3), indicating that there is little or no effect on the reaction of the two cyanate esters by altering their stoichiometry. However, an increase in both T_o and T_{exo}, as well as a decrease in ΔH_c is evident when compared to PT-30 (**1**), which is attributed to the complexity of the reaction, introduced by both homopolymerisation reaction and the slower copolymerisation (arising from the lower reactivity of the LECy component); this is consistent with previously published literature [22]. By means of comparison, Song *et al.* [23] examined the influence of carbon nanotubes on the cure kinetics of PT-30 to form nanocomposites and reported similar thermal characteristics (T_o = 217 °C, T_{exo} = 298 °C, ΔH_c = 667 J/g, including an initial cure of 501 J/g followed by a post cure of 166 J/g).

Using the DSC data (and assuming that full cure had been achieved during the first heat), the degree of curing was calculated for all blends using Equation 1.

$$\alpha = 1 - \frac{\Delta H_{pc}}{\Delta H_c} \qquad \textit{Equation 1}$$

where ΔH_{pc} and ΔH_c refer to the respective enthalpies upon post-curing and curing.

High degrees of curing were achieved, with values exceeding 0.95 for all blends (Table 3), which is particularly important where cyanate esters are concerned, since the deleterious effects of moisture and elevated temperatures in the formation of carbamates and subsequent decarboxylation to form blisters are well documented [24].

3.4 Kinetic analysis of the thermal polymerisation of the binary blends.

Changing the ramp rate of the DSC analysis allows for the determination of the activation energy (E_a) of the polymerisation reaction for the different blend families. The blends chosen for the specific study refer to the benchmark oligomer (**1**) and a binary blend [$\mathbf{1}_{85}$:$\mathbf{2}_{15}$], given that the combination of its properties is the most desirable within the series. DSC thermograms of each blend heated at heating rates of 5, 10, 15, and 20 K min^{-1} are provided (Fig. S2).

As expected, the effect of the increase in heating rate serves to shift the value of T_{exo} to higher temperatures in both blends. By considering the relationship between enthalpy and time (equation 2), conversion (α) plots against time for all systems were produced.

$$\boldsymbol{\alpha = \frac{\Delta H_t}{\Delta H_c}} \qquad \textit{Equation 2}$$

where ΔH_t and ΔH_c refer to the respective enthalpies at time *t* and upon complete curing. Both values are acquired by integrating the exothermic peaks of the thermograms. As demonstrated from Fig. 3, slower heating rates cause the completion of curing at lower temperatures. In agreement with the DSC thermograms, conversion results highlight an increase in cure temperatures through the incorporation of (**2**). Full conversion for the binary blend occurs below 360 °C.

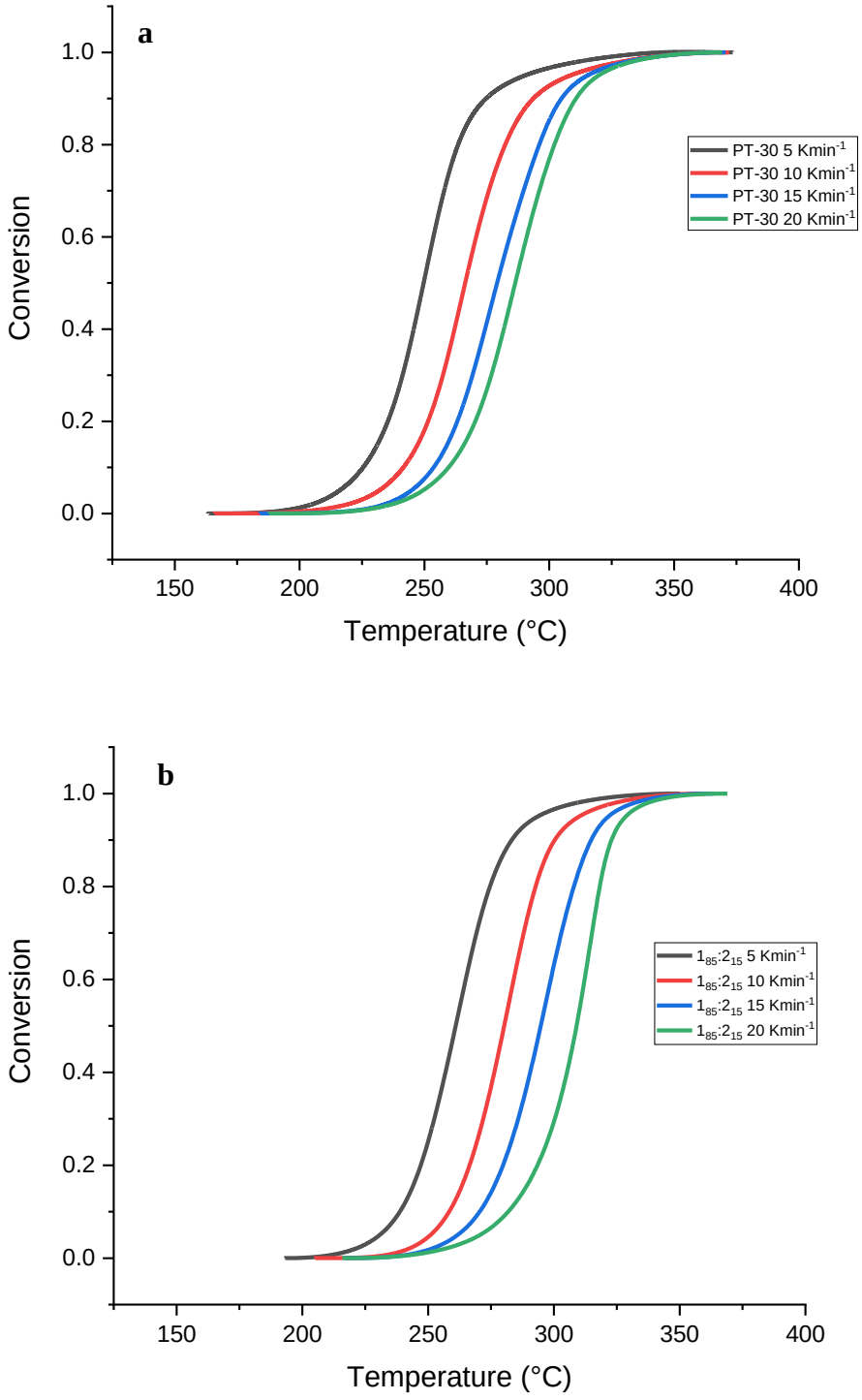


Figure 3: Conversion plots of selected compounds: **1** (**a**) and $\mathbf{1}_{85}$:$\mathbf{2}_{15}$ (**b**) at different heating rates.

The determination of the value of the E_a can be achieved *via* the use of a number of different models as summarized by Starink [25]. In the present study, the generalised Kissinger isoconversion method was used to calculate the E_a at each conversion fraction (Table 4).

Table 4: Kinetic data for the polymerisation of PT-30 (**1**), a binary blend $\mathbf{1}_{85}$:$\mathbf{2}_{15}$ calculated *via* the generalised Kissinger model.

Conversion	E_{act} *via* generalised Kissinger (kJ/mol)	
	1	$\mathbf{1}_{85}$:$\mathbf{2}_{15}$
0.1	78.6	67.9
0.2	81.7	64.6
0.3	82.5	64.0
0.4	82.5	64.4
0.5	82.2	66.0
0.6	81.7	67.6
0.7	81.0	70.5
0.8	82.1	75.1
0.9	93.8	84.7

It is immediately apparent, when considering all the uncatalysed blends, that (**1**) consistently displays the highest activation energy. The binary blends show similar profiles over the majority of the reaction pathway. Kinetic studies involving PT-30 are not as common as those featuring difunctional monomers [26, 27]. However, Crawford *et al.* [28,29] found that the enthalpy of polymerization (measured using dynamic DSC) ranged from 81.9 kJ/mol of cyanate group for PT-30 when uncatalyzed, to 90.3 kJ/mol of cyanate group when catalyzed with 300 ppm suspension of copper(II) acetylacetonate/dodecylphenol (1 % w/v). A binary blend of LECy and PT-30 (equivalent to $\mathbf{1}_{50}$:$\mathbf{2}_{50}$ in the current study) yielded an activation energy of 102 kJ/mol. using the Kissinger equation.

3.5 Dynamic mechanical analysis of the cured resin blends.

The analysis of PT-30 and similar high T_g resin systems presents some practical difficulties; not least because it often pushes the analytical equipment to its upper limits of operation. Furthermore, as discussed further below in connection with thermal stability, the determination of T_g may compete with the onset of thermal degradation, occasionally leading to blistering or slippage of the sample in the clamps. Nevertheless, the analysis of the cured sample of PT-30 displays a T_g (α transition) at 410 ^oC, based on the tan delta peak (Fig. 4), a subtle β transition at 220 ^oC, and a modest γ transition at 95 ^oC. In comparison, Walters *et al.* [31] reported a T_g of greater than 350 ^oC for PT-30, presumably due to the aforesaid limitations in instrumental capability. The binary blend $\mathbf{1}_{85}$:$\mathbf{2}_{15}$ was chosen for a comparative study and it displays a slightly higher storage modulus than the PT-30 reference, and the profile of the tan delta response is similar, with a β transition also falling at 220 ^oC. The drop in the storage modulus, heralding the start of the T_g, commences slightly earlier than PT-30 (at 300 ^oC), but reaches a peak maximum at a similar temperature.

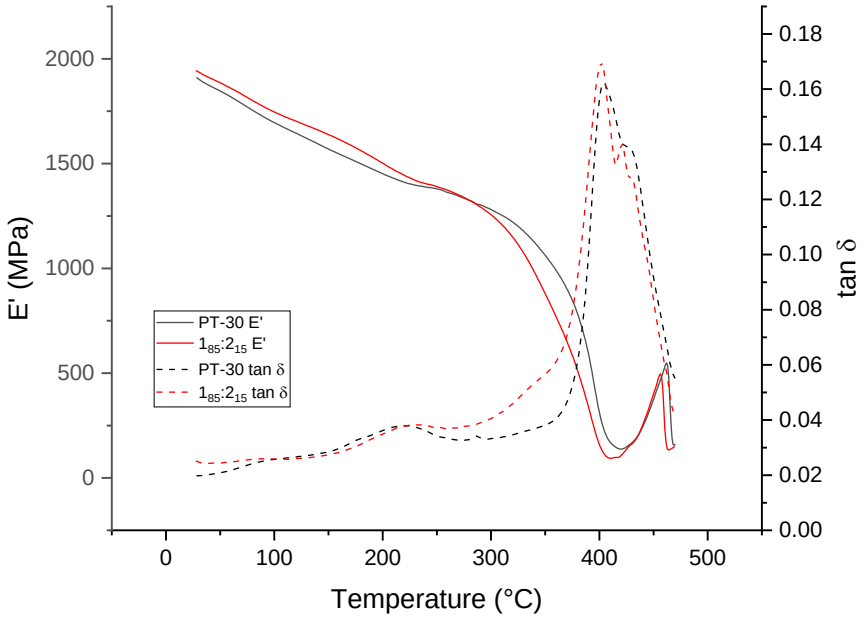


Figure 4: DMTA data for cured samples of PT-30 (**1**) a binary blend $\mathbf{1}_{85}$:$\mathbf{2}_{15}$.

3.6 Thermo-oxidative and thermal stability of cured resin blends.

Following cure, the resin blends were analysed for their thermal stability in nitrogen using STA and compared against PT-30 (**1**) as a baseline (Table 5). The cured LECy (**2**) is the least thermally stable of the materials studied with the lowest char yield, due to the presence of the ethylidene bridge containing a secondary hydrogen atom, the lowest aromatic carbon content and the comparatively low crosslink density. These TGA data compare favourably with those of Lyon *et al.* [30], who reported char yields (albeit at 900 ^{o}C) ranging from 50.5 % to 70.2 % for PT-30 and 30.2 % to 61.5 % for LECy (L-10 in that study) for heat fluxes of 100 to 35 kW/m^2 respectively. Walters *et al.* [31] also reported a char yields of 63 % (PT-30) and 47 % (L-10) using the TGA method, which agree still more closely with our data.

All of the blends show similar thermal stability up to initial mass loss of 5 wt%; the binary blends ($\mathbf{1}_x$:$\mathbf{2}_y$) containing at least, 75 wt% PT-30 (**1**), are comparable with PT-30 (**1**)

homopolymer up to a mass loss of 10 wt% (although other differences probably fall within the experimental error of the technique), but only the binary blends containing at least 85 wt% PT-30 (**1**) offer thermal stability of a similar order at mass losses of 20 wt %. The main deviations between the binary blends and Primset^{TM} PT-30 start to appear after mass losses of 20 %, although such temperatures greatly exceed the service temperature for which these blends are designed to be used. Once again, for comparison, Walters *et al.* [31] recorded a mass loss at 5 wt % for PT-30 at 457 ^{o}C. In general, within the current study a slight reduction in the thermal stability in observed following the incorporation of Primaset^{TM} LECy, which as a homopolymer displays a char yield (Y_c) at 800 ^{o}C some 20 % lower than that for Primaset^{TM} PT-30.

Table 5: TGA data for cured binary blends obtained in nitrogen.

System	$T_{5\%}$	$T_{10\%}$	$T_{20\%}$	$T_{30\%}$	Y_c	D1 (^{o}C) for 5 % mass loss
1	433	447	530	696	68	434
2	427	434	442	458	46	439
[$\mathbf{1}_{75}$:$\mathbf{2}_{25}$]	434	443	486	590	62	436
[$\mathbf{1}_{80}$:$\mathbf{2}_{20}$]	433	443	494	604	63	437
[$\mathbf{1}_{85}$:$\mathbf{2}_{15}$]	433	444	502	618	64	436
[$\mathbf{1}_{90}$:$\mathbf{2}_{10}$]	433	444	504	619	64	437
[$\mathbf{1}_{95}$:$\mathbf{2}_{5}$]	432	442	470	604	63	438

Key: $T_{x\%}$ = temperature at which mass loss of x% is recorded (^{o}C), Y_c = residual mass (char yield, %) recorded at 800 °C, D_1 = peak mass loss rate temperature (^{o}C)

Walters *et al.* [31] performed an in-depth study of the mechanisms of thermal degradation of a series of cyanate esters using a combination of spectral and thermal measurements. They

observed that the polycyanurates experienced little degradation at temperatures below 400 ºC, but above 400 ºC, thermal decyclization of the cyanurate to cyanate occurred with thermal isomerization of the cyanate to isocyanate (which subsequently reacts with moisture to form carbamates that can further hydrolyze to carbamic acid, an unstable intermediate). Above 475 ºC, cyanic acid (HOCN) was eliminated. Above 440 ºC, significant weight loss was observed for the polycyanurates until only the optically black char remains. This study was complementary to another reported study by Lyon [32] who examined the kinetics of char formation for PT-30 (along with the less thermally stable poly(methyl methacrylate) and polyethylene). Lyon reported that the Arrhenius rate constant for the thermolysis of primary chemical bonds in the PT-30 ranged from 1.4×10^{-5} s^{-1} (350 ºC) to 1.2×10^{-3} s^{-1} (450 ºC), with an activation energy of 178 kJ/mol ($A = l0^{9}$ s^{-l}).

In the present study, while the behaviour in nitrogen is informative, the application would see the materials exposed at elevated temperatures in air. Consequently, all of the cured binary blends were exposed to more demanding conditions as their thermo-oxidative stability was assessed in air during isothermal exposure at 250 ºC over an extended period of exposure (1536 hours) (Fig. 5). The homopolymer of Primaset^{TM} PT-30 (**1**) was included as the baseline, and the cured commercial polycyanurate loses 45.03 % of its mass after a period of 3048 hours' exposure. Of the binary blends, [$\mathbf{1}_{95}$:$\mathbf{2}_{5}$], containing the greatest amount of PT-30 (**1**), predictably displays a similar level of performance (48.34 % loss), but even when higher levels of LECy (**2**) are incorporated, similar levels of stability can be achieved up to periods of 400 hours.

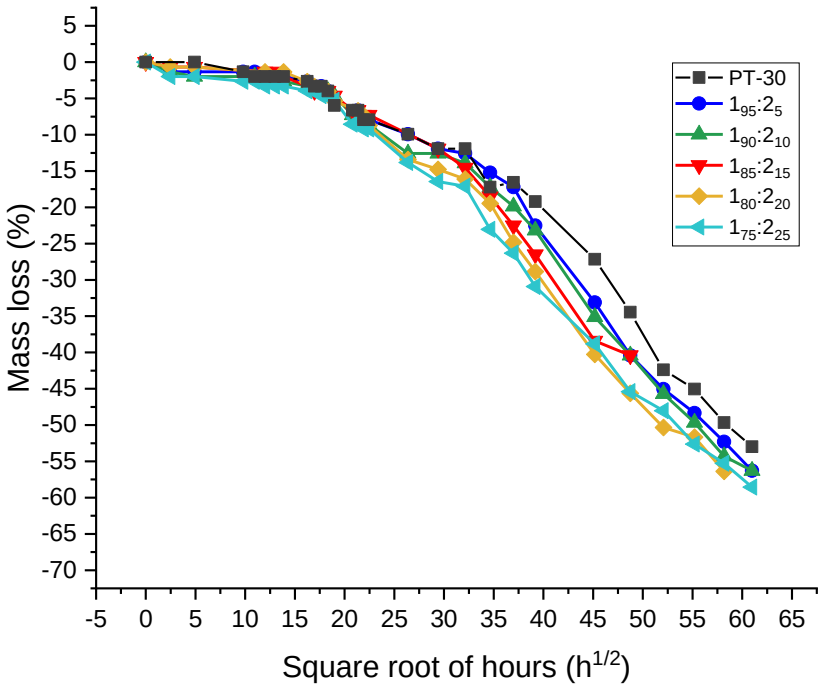


Figure 5: Thermo-oxidative stability for PT-30 (**1**) and binary $\mathbf{1}_x$:$\mathbf{2}_y$ blends when exposed in air at 250 ºC.

2.4. Determination of Moisture Uptake in Cured Resin Blends

Cured resin plaques for selected samples (PT-30 (**1**) and $\mathbf{1}_{80}\mathbf{2}_{20}$) were exposed to conditions of high temperature and high humidity (80 °C and 85% RH) for an extended period of time (3127 hours). Whilst the moisture absorption profiles do not reach equilibrium for these 2 mm thick samples) the plots for PT-30 and the binary blend suggest that a plateau is beginning to form (Fig. 6). The initial region of the absorption curves was found to be linear, characteristic of Fickian diffusion, and after the initial rapid uptake, the absorption process was comparatively slow. Of the two samples tested, Primaset™ PT-30 is the poorest performing, reaching a mass increase of over 5.22 wt % under these conditions. The introduction of the Primaset™ LECy (**2**) component with the more hydrophobic ethylidene moiety reduces the moisture uptake

significantly (a drop of around 0.36 wt %). Jones *et al.* [33] performed an extensive study of the moisture uptake characteristics of cyanate-epoxy copolymers and reported that one of the more important factors which determine the concentration of moisture that a polymer will absorb is the effect of non-random mixing whereby water-clustering is said to occur. They reported that Flory-Huggins theory was not able to predict accurately the isotherms observed for highly polar polymers since the theory assumes complete random mixing. In their studies, with complementary relative humidities of 40% R.H. and higher, the cluster size indicated that the majority of the water in a cured cyanate ester/epoxy blend is not clustered but is present as monomeric form, presumably hydrogen bonded to polar sites. Although the epoxy-containing networks will be more polar than either the Primaset^{TM} PT-30 homopolymer or the binary blends examined here, the same observations are relevant since a reduction in the number of hydrogen bonding sites results in a reduction in moisture absorption.

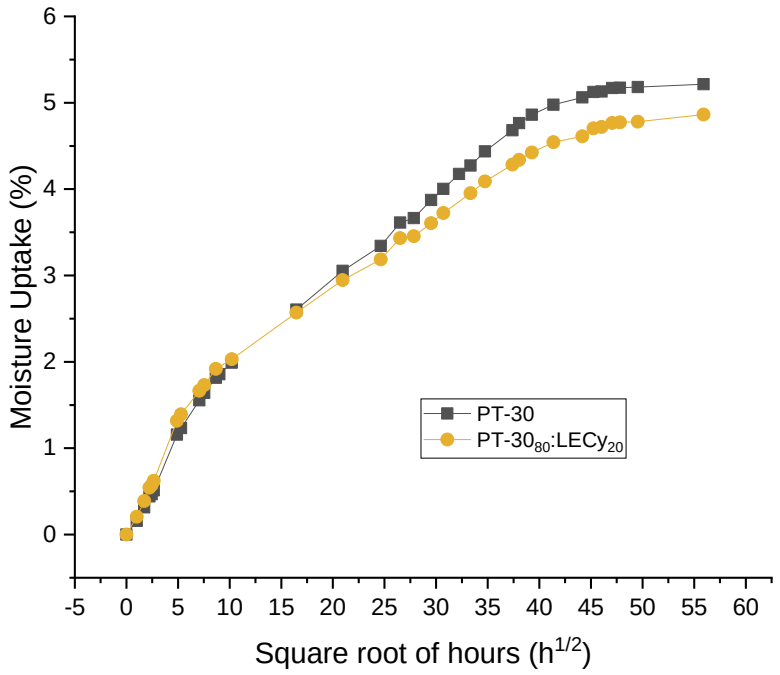


Figure 6: Moisture absorption profiles for PT-30 (**1**) (red) and selected a binary blend $\mathbf{1}_{85}$:$\mathbf{2}_{15}$ when exposed to 80 ºC, 85 % RH.

Previous work by Crawford *et al.* to examine binary blends of cyanate ester resins [34] investigated the influence of network crosslink density and the tortuosity of the path, on moisture ingress and egress and the resulting degradation mechanisms. They postulated that the formation of a more open, less crosslinked polycyanurate network might be responsible for the more rapid ingress and egress of moisture, leading to reduced moisture uptake and the DMTA data (Fig. 4) are consistent with this.

4. Conclusions

It has been shown here that the processing characteristics of a commercial phenolic-triazine (PT) resin can be improved significantly through the addition of relatively small quantities of a commercial low viscosity difunctional cyanate ester to achieve reactive binary systems. Throughout this work, the properties of the blends are compared against an industrial standard (Primaset^{TM} PT-30). It is found that blends containing 20-25 wt% LECy exhibit low viscosities (<1000 mPa.s) at 50 °C, making them suitable for liquid composite moulding processes. Dynamic differential scanning calorimetry is employed to monitor the cure reactions and the kinetics of the different reactions are analysed using the generalised Kissinger model to yield activation energies of 85 kJ/mol. For a conversion of 90%. The thermomechanical performances of the cured blends compare favourably with the industrial standard system (Primaset^{TM} PT-30, with the best performing systems exhibiting T_g values in excess of 300 °C based on the drop in

storage modulus (compared with value of at least 350 °C for PT-30). After conditioning for 3127 hours at 80 °C and 85% RH, a cured binary resin blend absorbed 4.9 wt% of moisture, compared with a figure of 5.2 wt % for Primaset^{TM} PT-30. When exposed to 250 ºC in air continuously over a period of 3048 hours, the best performing of the binary cured blends lose only 48.3 % of their mass, compared with 45.0 % for Primaset^{TM} PT-30 under the same conditions. The significant advances made here in improving the resin blends' processability open the door for their use in manufacture of fibre reinforced composites by liquid moulding techniques for the first time. The processability of the new resin blends and the mechanical properties of the resulting composites will be the subject of future studies.

AUTHOR INFORMATION

Author Contributions

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Data Access Statement

The data used in this study are not available due to commercial sensitivities.

Supporting Information

Additional data are supplied as supporting information.

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Abbreviations

CE, cyanate ester; PT, phenolic triazine, DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis.

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